# ABSORPTION OF ENERGY FROM HIGH FREQUENCY SOUND WAVES

BY
BHAGAT SINGH
B.S., University of Illinois, 1933
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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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# ABSORPTION OF ENERGY FROM HIGH FREQUENCY SOUND WAVES

## I. INTRODUCTION

The field of supersonics, inaudible sound, has acquired some importance in the past decade. The supersonic technique has been used for the measurement of absorption and dispersion, change of velocity with frequency, in a gas or a gaseous mixture.

An important problem in physics and chemistry is that of collisions and collision mechanisms. This technique, as a method of attack applied to a gaseous mixture, may eventually throw light upon the process involved in internal energy transfer when molecules of one gas collide with those of another.

As originally proposed, this work was initiated to investigate the absorption of sound in $O_2$ containing different amounts of $H_2O$ vapor. Since certain technical difficulties came in the way, it was decided to investigate $CO_2$, and mixtures of it with A, $H_2$, and $H_2O$ vapor.

## II. THEORY

The absorption of sound in gases, according to classical theory, depends only on the viscosity and thermal conductivity. The first sound absorption measurements in air were carried out by Neklepajew[1] for a range of frequency from 132 to 415 K.C. Further measurements were subsequently made in different gases by Pielemeyer[2], Grossman[3], and Abello[4]. With the exception of monoatomic argon, their results were considerably higher than those calculated theoretically,—inthe case of $CO_2$ as much as several hundred times; their measurements also showed that the absorption coefficient was not independent of frequency, a fact contradicted by the classical theory.

It is known today that the absorption of sound in polyatomic gases is conditioned by intramolecular processes, and that this molecular absorption is considerably greater than classical absorption. Kneses[5] and Bourgin[6] have simultaneously given the mathematical theory of the phenomenon, the latter author's theory being a logically complete analysis

of sound propagation in gaseous mixtures. The main features of Bourgin's theory may be outlined as follows.

1. At frequency, fm, a polyatomic gas has a region of maximum absorption corresponding to a set of internal states which figure in the transference of energy from and to the sound impulse.

2. The effect of an added active impurity—$H_2O$ vapor, $H_2$, etc.—is to shift the region of maximum absorption to a higher frequency.

3. At any frequency $f<fm$, the absorption decreases with increasing ocncentration of an impurity, while at $f>f_m$, absorption increases first, goes through a maximum, and then decreases with the addition of impurity.

4. An inactive impurity—A, He, etc.—has very little effect upon absorption.

5. At a given frequency the effect on absorption of decreasing the pressure is the same as if the frequency were increased.

## III. EXPERIMENTAL

The circuit used is essentially that of Pierce[7] except for the linear recording device, a vacuum tube voltmeter, which is connected across the crystal electrodes. The piezo crystal oscillator generates the following four frequencies: 30, 60, 90, and 120 K.C. The crystal and the electrodes are supported on a bakelite plate which is attached to the inside wall of a brass box (45x25x18 cm.). A ground glass plate fits the top of the box to make it air-tight, and the openings on the side of the box are connected to a differential mercury gauge and a vacuum pump. Perpendicular to the longitudinal axis of the crystal is a brass reflector (8x8 cm.) which is attached to a gear drive. The reflector can be moved back and forth by an electro-magnetic induction motor, and its position is indicated on an attached scale.

The box is filled with $CO_2$ dried over $P_2O_5$ and $H_2SO_4$ for several hours; the temperature and pressure of the gas is recorded. Water vapor is introduced by means of a trough containing a saturated solution of an inorganic salt of known vapor pressure. Commercial A and $H_2$ are dried and used as impurities.

When the crystal oscillates, standing waves are set up between the reflector and the crystal. The voltage across the electrodes is determined by the vibrations of the crystal and by the force of the incoming reflected

wave. As the position of the reflector is changed, the voltage amplitude across the electrodes goes through maximum and minimum values—the consecutive maxima and minima corresponding to reflector positions half a wave length apart.

To make the measurements, dry $CO_2$ or $CO_2$ and an impurity, is introduced into the air-tight box. The crystal is set oscillating, and the reflector is set about 2 cm. away from the crystal. As the reflector is moved away from the crystal, a distance of about twenty half wave lengths, the maxima and minima on the vacuum tube voltmeter are recorded and the reflector positions corresponding to these maxima and minima noted.

The calculation of absorption coefficient is as follows. Assume that the voltage across the crystal electrodes, E, is proportional to the pressure at the crystal surface and the plane wave makes a single round-trip between the crystal and the reflector; then the pressure, p, at any point along the path of the wave is

$$p = p_0 \quad e^{-\alpha L} \quad \sim_E,$$

where

$p_0$ = pressure at the crystal surface

$\alpha$ = pressure absorption coefficient / cm.,

and $L$ = distance travelled by the wave in one round-trip (twice the distance between the reflector and the crystal). Then

$$\alpha = \frac{2.3 \log p^1/p^2}{(L_2 - L_1)} = \frac{2.3 \log E_1/E_2}{(L_2 - L_1)}$$

The absorption coefficient for intensity / cm., m, is $2\alpha$, and the absorption coefficient / wave length, $\mu$, is $m\lambda$, where $\lambda$ is the wave length.

A plot of voltmeter readings against L is made from which a logarithmic plot is constructed. The absorption coefficient is calculated from the above formula.

## IV. RESULTS

TABLE 1

A. Absorption versus frequency for dry $CO_2$

| $f_{K.C.}$ | $P_{CO_2}$ m.m. | T°C | $\alpha$ | m | $\mu$ |
|---|---|---|---|---|---|
| 30 | 749 | 26 | 0.083 | 0.17 | 0.153 |
| 60 | 741 | 27.5 | 0.235 | 0.396 | 0.226 |
| 90 | 741 | 28 | 0.56 | 1.12 | 0.342 |
| 120 | 740 | 29 | 0.54 | 1.08 | 0.248 |

TABLE 2

B. $H_2O$ as an impurity

| $f_{K.C.}$ | $P_{CO_2} + H_2O$ m.m. | % $H_2O$ | T°C | m | $\alpha$ | $\mu$ |
|---|---|---|---|---|---|---|
| 120 | 731 | 0.48 | 29 | 0.349 | 0.698 | 0.159 |
| 120 | 741 | 1.62 | 28 | 0.334 | 0.668 | 0.151 |
| 120 | 740 | 1.8 | 28 | 0.29 | 0.58 | 0.133 |
| 120 | 743 | 2.2 | 27.5 | 0.116 | 0.232 | 0.052 |

TABLE 3

C. $H_2$ as an impurity

| $f_{K.C.}$ | $P_{CO_2} + H_2$ m.m. | % $H_2$ | T°C | $\alpha$ | m | $\mu$ |
|---|---|---|---|---|---|---|
| 120 | 740 | 1.42 | 29.5 | 0.416 | 0.835 | 0.19 |
| 120 | 740 | 2.7 | 28 | 0.418 | 0.836 | 0.192 |
| 120 | 740 | 5.4 | 27.5 | 0.295 | 0.59 | 0.137 |
| 120 | 740 | 8.1 | 28.5 | 0.256 | 0.312 | 0.12 |

TABLE 4

D. A as an impurity

| $f_{K.C.}$ | $P_{CO_2} + A$ m.m. | % A | T°C | $\alpha$ | m | $\mu$ |
|---|---|---|---|---|---|---|
| 90 | 743 | 2.7 | 27 | 0.49 | 0.98 | 0.3 |
| 90 | 742 | 5.4 | 27 | 0.45 | 0.9 | 0.276 |

TABLE 5
Pressure versus Absorption

| $f_{K.C.}$ | $P_{CO_2}$ m.m. | T°C | m | $\mu$ | log f/p $\left(\begin{matrix}f = \text{K.C.} \\ P = \text{atm.}\end{matrix}\right)$ |
|---|---|---|---|---|---|
| 90 | 738 | 26 | 0.8 | 0.242 | 1.967 |
| 90 | 635 | 26 | 0.632 | 0.191 | 2.032 |
| 90 | 535 | 26 | 0.656 | 0.198 | 2.106 |
| 90 | 432 | 26 | 0.703 | 0.212 | 2.2 |
| 90 | 332 | 26 | 0.803 | 0.246 | 2.313 |
| 90 | 231 | 26 | 0.963 | 0.298. | 2.471 |
| 90 | 130 | 26 | 1.103 | 0.34 | 2.72 |

## V. DISCUSSION OF RESULTS

The results are summarized in Tables 1, 2, 3, 4, and 5.

From a plot based upon data of Table 1, it can be shown that the absorption coefficient has a maximum value of 0.35 at a frequency of 100 K.C. If the heat capacity is calculated from valence and bending vibrations of the $CO_2$ molecule, and this value used to calculate the maximum absorption, $\mu_{MAX.}$, it comes out to be 0.34. This value compares favorably with the experimental value of 0.35. This shows that the bending and valence vibrations are active in energy exchanges which accompany collisions between $CO_2$ molecules, and it is the loss of their heat capacity which is responsible for the absorption of energy from the sound wave. The assymetrical vibration contributes very little to the heat capacity at room temperatures.

The introduction of increasing concentration of $H_2O$ and $H_2$ lowers the absorption, as is evident from Tables 2, and 3. A smaller amount of $H_2O$, as compared with $H_2$, produces a given lowering. This lowering is brought about by the following fact: a collision between a $CO_2$ molecule and a molecule of $H_2O$ or $H_2$ is much more effective in transferring of energy between excited and unexcited molecules than is a collision between two $CO_2$ molecules. However, the introduction of A does not affect the absorption. Eucken and Becker[8] have postulated chemical affinity between the molecules of the gas and those of an impurity, to account for the effectiveness of collisions.

Table 5 indicates that a lowering of pressure increases absorption,

a fact which is in direct contradiction to the theory developed by Bourgin. It will be necessary to check this result by a more direct absorption method before any significance can be attached to it.

## VI. SUMMARY

The absorption region of $CO_2$ has been located, and it has been shown that the maximal absorption occurs at a frequency of 100 K.C. The elimination of the vibrational heat capacity due to the bending and symmetrical valance frequencies has been shown to be the cause of this absorption maximum.

The effect of active impurities, like $H_2O$ and $H_2$, is to decrease the absorption and to shift the maximum of absorption to higher frequencies. It has been shown that $H_2O$ is more effective in the lowering of absorption than $H_2$. Inert gases, like A, seem to have no effect on absorption. Finally, it has been shown that absorption increases with decrease in pressure of $CO_2$.

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## VITA

The author was born near Jullundur, Punjab, India, on April 11, 1912. After finishing the local High School, he attended the University of California for three years, and then transferred to the University of Illinois, from which he got the B.S., and M.S. degrees in 1933 and 1934, respectively. Since September, 1935, he has been a graduate student in the Chemistry Department. He is a member of Sigma Xi.

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